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CHEMICAL THERMODYNAMICS OF MATERIALS AT HIGH TEMPERATURES

Technical Report No. 13

SOLID SOLUTION EQUILIBRIA IN THE ZIRCONIUM-HYDROGEN SYSTEM

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By R. K. Edwards, P. Levesque,[1,2] and D. Cubicciotti[3]

(1) Based on part of a thesis submitted by Pascal Levesque to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1953.

(2) Presently at Metallurgy Department, Sylvania Electric Corporation, Ipswich, Massachusetts.

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ABSTRACT

The solubility of hydrogen in zirconium has been determined as a function of temperature and hydrogen pressure in the temperature range 600° to 900°C. The solubilities obtained for a hydrogen pressure of one atmosphere are about ten per cent higher than those obtained by Hall, Martin, and Rees.[9]

A partial binary phase diagram is presented and correlated insofar as possible with previous x-ray work. In particular, we have indicated existence of a new phase, δ, in the composition range 59.4 to about 61 atom per cent hydrogen. The zirconium-rich boundary of this phase is invariant with temperature. This phase is apparently separated from the ε phase (which includes the composition ZrH_2) by a very narrow two-phase field which has generally escaped detection and was only indirectly established in this paper.

* * * * *

INTRODUCTION

The phenomenon of extensive interaction of hydrogen with many of the transition metals[4] to form products of metallic behavior affords a

(4) For a review of the very extensive literature on the subject and an essentially complete bibliography up to 1947, see D. P. Smith, "Hydrogen in Metals", The University of Chicago Press, Chicago (1948).

unique opportunity for study of special aspects of metallic bonding. That the molecularity of hydrogen is broken down as the gas enters the metal was first established by Hoitsema and later amply verified when it was shown that the initial hydrogen solubility was proportional to the square root of the hydrogen pressure.[4] Rundle, Shull, and Wollan's[5] recent neutron

(5) R. E. Rundle, C. G. Shull, and E. O. Wollan, Acta Cryst., 5, 22 (1952).

diffraction studies on the high hydrogen composition phases ThH_2 and ZrH_2 have located the atomic sized particle in slightly flattened metallic tetrahedra. Coehn and coworkers demonstrated, moreover, that the particle in the case of Pd-H was the proton, as the dissolved hydrogen was found to migrate towards the cathode on passage of an electric current.[4] Palladium, thorium, and zirconium lose their paramagnetism on solution of hydrogen by the time compositions $PdH_{0.66}$, ThH_2, and ZrH_2, respectively, are reached;[4,5,6]

(6) J. Fitzwilliam, A. Kaufmann, and C. Squire, J. Chem. Phys. 9, 678 (1941).

consequently the protonic nature of the hydrogen is supported, and in short hydrogen in these metals appears to be metallically bonded in the usual sense. Pauling and Ewing[7] have obtained a "metallic" radius of 0.27A

(7) L. Pauling and F. J. Ewing, J. Am. Chem. Soc., 70, 1660 (1948).

for hydrogen. Wigner and Huntington[8] have calculated theoretically for a

(8) E. Wigner and H. B. Huntington, J. Chem. Phys. 3, 764 (1935).

body-centered cubic "metallic" hydrogen, a cohesive energy of 10.6 Kcal. per gram-atom and a density of 0.59 grams per cc.

Several of the interpretations of physical measurements in the Zr-H system have been unsatisfactory because of the lack of knowledge of the phase equilibria behavior in the solid system. The present investigation was conducted for the purpose of determining the relevant binary phase diagram, with the immediate objective of establishing suitable reference conditions for a study since conducted on the ternary Zr-O-H system. The

study was by the method of measurement of the equilibrium hydrogen pressure in a series of isothermal observations as the composition of the solid was varied by successive additions of measured volumes of hydrogen. Preliminary measurements had indicated some ten per cent discrepancy from the work of Hall, Martin, and Rees,[9] who carried out a similar investigation. Related

(9) Mrs. M. N. A. Hall, S. L. H. Martin, and A. L. G. Rees, Trans. Faraday Soc., 41, 306 (1945).

measurements at very low hydrogen compositions have been reported by de Boer and Fast.[10]

(10) J. H. de Boer and J. D. Fast, Rec. Trav. Chim., 55, 350 (1936).

EXPERIMENTAL

Apparatus: A schematic drawing of the experimental apparatus is shown in Figure 1. The vacuum pumping system consisted of a mechanical pump, a two-stage mercury diffusion pump, and a dry ice-chloroform-acetone trap for condensible gases. Vacuum pressures were measured by means of an ionization gauge isolated from mercury vapor and other condensible gases by a liquid nitrogen trap.

The hydrogen purification train consisted of (1) a furnace-heated quartz glass tube filled with five per cent platinized asbestos and operated at 225°C.; (2) a ten-inch spiral trap at liquid nitrogen temperature; and (3) a furnace-heated quartz glass tube filled with fine zirconium metal turnings and held during operation at a temperature of 800°C. A 100 ml. water-jacketed gas burette was used in conjunction with a mercury leveling bulb for gas volume measurements. The burette was graduated to 0.2 ml. and readings were estimated to 0.05 ml. The position of the leveling bulb was controlled by a counterbalance weight and pulley arrangement. Volume measurements were made at atmospheric pressures as determined by a null reading on the open-arm manometer. Atmospheric pressure measurements were read on an external laboratory manometer. A thermometer graduated to 0.1 ml. was in the water jacket of the burette and another similar thermometer was taped to the glass tubing in a position to register any temperature fluctuation in the gas volume region not within the burette. The temperature

of the gas volume system was held constant during measurements to ± 0.1°C. by use of a combination heater-cooler air circulating fan.

The reaction chamber was an 8 mm. quartz glass tube and the sample inside was additionally contained in a small alumina thimble. The sample was introduced at the pyrex end (a graded seal connected this to the quartz glass section) and slid down into an alumina boat when the quartz glass tube was tipped downward. The tube was then sealed and returned to the horizontal position. The tipping operation was accomplished as the appropriate glass section was worked at suitable temperature. A calibrated chromel-alumel thermocouple was placed outside the quartz tube with its junction directly beside the specimen. A porcelain tube was then placed around the assembly and fitted through a firebrick into a resistance furnace. A Leeds and Northrup Micromax recorder-controller, acting on the signal from a thermocouple near the furnace windings, served to regulate the furnace temperature within such a tolerance that the sample zone itself could be held to ± 1°C. A Rubicon precision potentiometer was used to measure the millivoltage of the sample zone thermocouple. The major portion of the apparatus was shielded from furnace heat by a framework of aluminum foil-lined asbestos panels. The furnace was mounted on wheels which ran along tracks and safe movement back and forth to a reproducible operating position was achieved simply.

The equilibrium hydrogen gas pressures over the sample were read on a manometer shown schematically in Figure 1 as a closed-end manometer, but its closed end section actually was connected to the high vacuum section through a stopcock. Pressures were estimated to ± 0.5 mm. of mercury.

MATERIALS

The zirconium was in the form of wire of 0.015 inch diameter and was obtained from the Foote Mineral Company. The analysis supplied with the material was 2.5-3.0% Hf, 0.04% Fe, 0.03% O, and 0.01% N.

Commercial hydrogen was purified by passing it over shredded five per cent platinized asbestos heated to 225°C. and then through the trap section at liquid nitrogen temperature to remove all traces of water. Finally the hydrogen was passed through zirconium turnings at 800°C. to getter impurities such as nitrogen, carbon dioxide, or any remaining oxygen or water vapor. The turnings on cooling in the hydrogen atmosphere would take up a considerable quantity of hydrogen which could later be liberated for experimental use as

desired on reheating the turnings. In some cases the gas was used directly as it passed slowly through the purification train.

PROCEDURE

About fifty milligrams of zirconium wire were used in a typical determination of a pressure-composition isotherm. The wire was cleaned by abrasion with 2/0 emery paper, weighed, and introduced into the apparatus. The system was evacuated for at least eighteen hours and to a pressure of 10^{-5} mm. of mercury. Then hydrogen was flushed through the system twice, following which the sample was brought rapidly to the desired temperature in the presence of hydrogen, at a pressure of about 300 mm. of mercury. The system was next evacuated for fifteen minutes to free the sample of hydrogen, and the determination of an isotherm was commenced. The rate of absorption of the hydrogen nearly always was very fast. In any case in which this was not so, the run was discontinued and a new sample was introduced. As a standard procedure, after each successive addition of hydrogen the equilibrium was considered to prevail if no more than 0.5 mm. of change in pressure occurred within ten minutes. Check observations over longer periods of time showed this practice to be reliable. X-ray diffraction patterns were taken on both the original wires and on the residual specimen wires after they had been fully saturated with hydrogen at a given temperature and under a hydrogen pressure of one atmosphere and additionally cooled in the presence of hydrogen at one atmosphere pressure.

The error in the measurements is estimated to be ± 1.0 mm. of mercury in the pressure, ± 1.0°C. in the temperature, and ± 1.5 ml. of hydrogen per gram of zirconium in the composition. Correction of the composition for the amount of hydrogen remaining in the reaction zone gas phase was accomplished through comparison with a complete series of blank determinations made in the absence of a sample and at all temperatures and pressures.

RESULTS

The experimental pressure-composition isotherms are shown in the following figures with the estimated determinant experimental error represented by the size of the data points. Figure 2 is perhaps the most illustrative and shows isotherms of the hydrogen gas pressure plotted against the number of milliliters of hydrogen gas taken up per gram of zirconium metal. Figures 3 and 4 show similar isotherms at the additional temperatures 885°C., 865°C.,

860°C., and 855°C., which were supplementally determined with special emphasis on searching for the α-β zirconium transformation as will be apparent later in the discussion. The latter plots were made on separate figures to reduce overcrowding of the data. In Figures 5 and 6 all of the data have been replotted, logarithm of hydrogen pressure versus logarithm of hydrogen composition in atom per cent. The log-log form of plotting provides a higher degree of linearity by smoothing simple power and exponontial dependencies. In the least, such plots permit a consistent extraplation to phase field boundaries and have been used to obtain the phase boundary data listed in Table 1, and the data plotted in the partial phase diagram shown in Figure 7. The shaded area to the right side of the latter figure represents a temperature-composition region corresponding to hydrogen pressures in excess of one atmosphere and not investigated in this study. The regions for which we have only indirect evidence are shown bounded by dashed lines. Table 2 lists the isobaric solubility of hydrogen in zirconium as a function of temperature and at a pressure of 760 mm. of Hg.

Table 3 lists pressure-temperature data for some pertinent compositions, taken from the smoothed pressure-composition isotherms. These data have been plotted with the logarithm of the pressure versus the reciprocal absolute temperature in Figure 8, and the derived partial molal heat of solution data for molecular hydrogen in zirconium have been listed in Table 4, together with the corresponding partial molal entropy of solution.

The experimental data for all isotherms have been tabulated for reference in Table 5.

DISCUSSION

The partial phase diagram shown in Figure 7 has been deduced for the temperature interval between 700 and 900°C. The symbols for identification of phases have been selected with as logical a correspondence as possible to those used by Hägg[11] in his x-ray studies. Hägg's conclusions have been

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(11) G. Hägg, Z. physik. Chem., 11B, 433 (1931).

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criticised by Smith. It is to be borne in mind that all of the x-ray studies were conducted at room temperature, several hundred degrees lower

than the present work.

The low temperature allotrope of Zr has been customarily designated as the α-modification. It transforms at 865°C. from its hexagonal close-packed symmetry to a phase designated as the β-modification with body-centered cubic symmetry. In the binary diagram we have similarly labeled what we believe to be the corresponding primary solid solution fields in the Zr-rich regions. The ε-phase, which approaches the composition corresponding with ZrH_2 at the highest hydrogen compositions, was reported to be face-centered tetragonal by Hägg. Rundle, Shull, and Wollan[5] interpreted their x-ray and neutron diffraction results on this phase to indicate that it was body-centered tetragonal, but they established through equivalence of interplanar distances that they were dealing with the same phase as that designated ε by Hägg. Our x-ray diffraction measurements established clearly the equivalence of our ε-phase and that of Hägg. We have no evidence of the existence of the phase at Zr_2H which Hägg designated γ, but Jack[12] has recently indicated that he has encountered a face-centered tetragonal phase of such a composition in the case of 300°C. preparations cooled rapidly to room temperature. Annealing at 300°C. seemed to cause the disappearance of the phase.

(12) K. H. Jack, Private Discussion, Illinois Institute of Technology, July 28, 1953.

We obtained no direct evidence in this binary study as to the existence of the phase we have designated δ. However, in an investigation of the ternary Zr-O-H system which we have subsequently conducted, we have clearly encountered a reasonably wide ($\delta + \varepsilon$) two-phase region, which becomes increasingly narrow as the composition approaches that of the binary system.

From the nature of the ternary diagram it is apparent that the ($\delta + \varepsilon$) two-phase field must exist in the binary system, and a reasonable extrapolation leads to estimated two-phase compositions of a range of about 61 to 62 atom per cent hydrogen at 750°C., but the composition range could easily be more narrow. Such a very narrow isothermal invariant region would not be detected in our binary measurements. It seems that the region probably extends to at least as high a temperature as 850°C. In the ternary system there is evidence of joining of the ($\alpha + \delta$) and ($\delta + \varepsilon$) regions at temperatures of

about 860°C. The present investigation places the zirconium-rich boundary of the δ -phase at 59.4 atom per cent hydrogen and indicates this boundary is invariant with temperature. The high-hydrogen composition boundary is probably at about 61 atom per cent hydrogen.

We used the designation δ on the supposition that the phase should probably be identified with Hägg's δ -phase of face-centered cubic symmetry, which was presumed however to correspond to a composition of approximately ZrH. We have done so in view of analogy based on the report of Sidhu and McGuire[13] who found a face-centered cubic phase in the hafnium-hydrogen

(13) S. S. Sidhu and J. C. McGuire, J. App. Phys., 23, 1257 (1952).

system in the single phase composition region 63.0 to 64.8 atom per cent hydrogen. It is seen from Figure 7 that extrapolation of the (α + δ) two-phase field boundaries to the temperature of Hägg's x-ray studies would indicate that his presumed approximately ZrH compound would lie well out in the (α + δ) two-phase field so he would have observed some of the δ -phase. In fact, if linear extrapolation of the two-phase field boundaries could be assumed reasonable, it would lead to an estimation that about forty per cent of the two-phase mixture would be the δ -phase at a composition nominally corresponding to ZrH.

The (α + β) two-phase region was drawn in on the basis of the knowledge of the α - β transformation temperature for the pure metal and the character of the join of the zirconium-rich boundary of the (β + δ) and (α + δ) regions. Special supplementary runs were carried out in the temperature interval between 850°C. and 875°C. with composition changes being conducted in small steps with a view to finding the invariant isothermal pressure region corresponding to the α - β transformation. Within our experimental error, we were unable to observe the anticipated behavior and we conclude that the (α + β) field is probably very narrow in the direction of the temperature ordinate and that the α - β transformation takes place in the very limited temperature interval between 865°C. and 850°C. or less.

That the transformation temperature is lowered initially on addition of hydrogen was well established by de Boer and Fast[10] in their low pressure-low hydrogen composition studies. The conclusion of Fitzwilliam, Kaufmann, and Squire[6] that uptake of hydrogen by zirconium lowers the α - β transformation temperature by as much as 200°C. was based on the observation of

the magnetic susceptibility as a function of temperature of a sample being heated in hydrogen at one atmosphere pressure. They noted that at about 700°C. the magnetic susceptibility increased rapidly with temperature in a manner analogous with the behavior for the pure metal at the $\alpha - \beta$ transition temperature, and that the hydrogen uptake began slowly. However, they were surprised to find the susceptibility to fall off rapidly with temperature thereafter, whereas the magnetic susceptibility of the pure metal had remained nearly constant with temperature after the $\alpha - \beta$ transition. It is easy to see why the falling off in the case of the metal with hydrogen since it would have been taking up hydrogen and transforming towards the $\mathcal{E}$ -phase. The considerable, apparent lowering of the $\alpha - \beta$ transformation temperature is not in accord with the present work and considerably weakens our case for assuming the $\alpha - \beta - \zeta$ eutectoid join to be in the temperature region 850° to 860°C. Those authors did not list any composition data for the measurements just mentioned, but one would assume that the presumed transformation took place at very low hydrogen content. If this were true, then the $(\alpha - \beta)$ region should be shown dropping precipitously in our diagram. Our work requires that the region either be close in composition to the pure metal (in which case we could not have detected it in our isotherms since pressures would have been too low) or too narrow to detect on our isotherms.

One aspect of the work of Fitzwilliam, Kaufmann, and Squire is in agreement with predictions one would make, assuming the correctness of our diagram. Their three room temperature magnetic susceptibility measurements for compositions intermediate between Zr and ZrH_2 are linear with composition within experimental error though these authors did not comment on this point. The compositions of the materials measured lie very close to those which we would give for the $(\alpha + \delta)$ region plus part of the narrow δ -region, at room temperature, and certainly linearity would not be surprising here.

The partial molal molecular heat of solution of hydrogen gas in the zirconium-hydrogen solid solutions seems relatively constant at -39.6 Kcal. in the solid composition range 39.4 to 62.0 atom per cent hydrogen, except for the $(\alpha + \delta)$ two-phase field where the value is -49.6 Kcal. The latter would also be the heat of the reaction.

$$\alpha \text{ (solid saturated with Hydrogen)} + H_2(g) \rightarrow \delta \text{ (solid saturated with Zr)}$$

We found no sensible variation in these values with temperature regardless of whether different phases were involved, except for the highest compositions.

Hildebrand and Scott[14] have discussed intermetallic solid solutions

(14) J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes, (Reinhold Publishing Corp., New York, 1950).

in an extension of their treatment of solution theory. They have shown how some of the underlying assumptions of the development may be assumed to hold with greater validity with intermetallic solutions, giving numerous examples and tabulating the solubility parameters, where they have listed a value of 94 units for zirconium metal.

We have used the results of the cohesive energy and density calculations of Wigner and Huntington[8] to calculate a solubility parameter of 79 units for metallic hydrogen. We have also used the above cohesive energy in conjunction with the metallic radius for hydrogen given by Pauling and Ewing[7] and have obtained a solubility parameter of 117 units. One might select the mean value, 98 units, as representative for metallic hydrogen. The proximity of this value of the parameter to the value of the parameter for zirconium is of notable interest in that taken alone it would predict wide solid solubility for the zirconium-hydrogen system. That rather extensive solution does apparently occur might otherwise seem startling in view of the general lack of fulfillment of the conditions for complete solid solubility of metals as listed by Hildebrand and Scott.[14]

The initial slopes of the plots in Figures 5 and 6 are essentially 2 as would be expected, assuming solution of atomic hydrogen according to Henry's law. This is simply another way of noting that the initial hydrogen solubility varies as the square root of the molecular hydrogen pressure, commonly found as mentioned in the introduction to this paper.

It is to be recognized that the diagram presented may well be additionally incomplete in that the method is unsatisfactory for detection of very narrow two-phase fields or those occurring at very low pressures unless a more sensitive gas pressure and volume measuring apparatus is used. However,

we believe that the diagram presented here should provide a somewhat sounder basis for future investigations into the solid state chemistry of the system. In particular one should be alerted to the possible existence of narrow two-phase fields rather than the more usual case of narrow single-phase fields.

The values which we obtained for the total uptake of hydrogen by zirconium for a given pressure of one atmosphere were about ten per cent higher than those given by Hall, Martin, and Rees.[9]

Table 1. Boundary Compositions of the ($\alpha + \delta$) and ($\beta + \delta$) Two-Phase Fields in the Zirconium-Hydrogen System

Temperature °C.	Log_{10} Atom % Hydrogen		Atom % Hydrogen	
700	1.690	1.775	49.0	59.6
750	1.695	1.770	49.6	58.9
800	1.700	1.775	50.1	59.6
825	1.702	1.774	50.4	59.4
850	1.705	1.773	50.7	59.3
860	1.712	1.773	51.5	59.3
865	1.715	1.773	51.9	59.3
875	1.718	1.773	52.2	59.3

Table 2. Solubilities of Hydrogen in Zirconium at a Pressure of 760 mm. of Mercury

Temperature °C.	Volume H_2 Gas Occluded cc. at N.T.P./g. of Zr	Atom % Hydrogen
600	237	65.9
700	229	65.1
750	220	64.2
800	213	63.4
825	207	62.8
850	202	62.2
860	194	61.2
875	190	60.7
885	136	52.6
900	131	51.6

Table 3. Equilibrium Hydrogen Pressure (mm. of Mercury) for Various Hydrogen Compositions

Temperature °C.	HYDROGEN COMPOSITION, ATOM %							
	39.4	42.3	44.9	47.2	55.0	60.7	62.0	63.1
600	-	-	-	-	-	5	12	54
700	4	5.5	7.5	11	12	36	77	247
750	10.5	15	21	30	40	98	245	500
800	27	35	51	76	127	225	450	695
825	42	55	78	120	220	378	620	-
850	60	83	123	174	360	520	737	-
860	73	100	145	212	450	675	-	-
865	80	110	158	242	507	-	-	-
875	92	128	184	263	608	760	-	-
900	130	180	252	355	-	-	-	-

Table 4. Partial Molal Heats and Entropies of Solution of Molecular Hydrogen in Zirconium-Hydrogen Solid Solutions.

Composition Atom % Hydrogen	$\overline{\Delta H}$ Kcal./mole	$\overline{\Delta S}$ cal./mole/deg.
39.4	-39.6	-30.2
42.3	-39.6	-30.9
44.9	-39.6	-31.6
47.2	-39.6	-32.3
55.0	-49.6	-42.7
60.7	-39.6	-34.6
62.0	-39.6	-36.4

Table 5. Experimental Data. Equilibrium Hydrogen Pressures as a Function of Hydrogen Composition and of Temperature

Pressure mm.Hg	Atom % Hydrogen
(Aa*-600°C.)	
0	34.3
0	47.5
0	55.7
3	60.6
21	62.4
63	63.3
207	64.0
408	64.9
600	65.5
746	65.9
(Bb-600°C.)	
0	37.0
1	55.8
38	62.9
197	64.0
374	64.6
534	65.0
727	65.5
(Ac-700°C.)	
3	34.6
9	47.2
11	55.7
17	59.5
55	61.7
148	62.6
326	63.6
528	64.4
744	64.8
(Cd-700°C.)	
4	38.6
76	61.7
306	63.1
(Ae-750°C.)	
7	30.4
17	42.4
31	47.2
37	54.6
50	58.7
79	60.5
195	62.0
399	62.6
573	63.4
757	64.2

Pressure mm.Hg	Atom % Hydrogen
(Cf-750°C.)	
4	29.5
26	46.7
66	59.5
198	61.2
498	62.9
(Ag-800°C.)	
11	27.0
37	42.6
77	47.4
115	49.4
129	55.3
131	58.8
161	60.0
290	61.2
426	62.0
553	62.7
746	63.4
(Dh-800°C.)	
15	32.5
130	53.6
304	60.9
479	62.0
(Ai-825°C.)	
21	28.4
37	38.0
67	43.9
100	46.4
167	48.7
199	49.9
223	57.3
277	59.9
401	61.0
575	61.7
739	62.5
(Dj-825°C.)	
34	37.5
91	46.0
180	48.9
256	59.2
491	61.3
628	62.1

Pressure mm.Hg	Atom % Hydrogen
(Ak-850°C.)	
20	25.6
57	39.0
101	44.2
175	47.2
280	49.6
351	50.7
361	56.1
410	59.8
543	61.0
669	61.7
746	62.2
(El-850°C.)	
29	30.2
92	42.8
228	48.4
363	50.6
360	58.2
404	59.5
521	60.6
728	61.6
(Cm-850°C.)	
528	60.7
(An-855°C.)	
10	19.3
22	26.9
31	31.1
44	35.1
61	38.8
79	40.5
98	42.7
116	43.6
140	44.8
169	45.7
195	46.6
(Ao-860°C.)	
10	18.2
20	24.4
30	29.2
39	32.2
52	35.9
71	39.0
88	41.3
112	43.2
135	44.5
160	45.5
189	46.4
223	47.4
265	48.3
296	49.0

Pressure mm.Hg	Atom % Hydrogen
(Cp-860°C.)	
31	30.5
110	43.6
200	47.3
303	49.2
399	50.7
454	56.0
576	59.9
605	60.2
736	60.7
(Bq-865°C.)	
15	20.5
83	40.5
139	44.0
205	46.4
273	47.6
334	49.1
418	50.6
456	50.8
482	51.0
503	53.7
509	57.0
550	59.0
607	59.3
671	59.8
738	60.0
(Ar-875°C.)	
27	25.0
54	33.8
85	38.6
141	42.9
(As-875°C.)	
137	43.4
241	46.6
349	49.1
461	50.7
522	51.3
562	51.5
600	54.8
(At-875°C.)	
250	46.8
558	51.6
611	53.2
614	59.0
649	60.1
738	60.6

Pressure mm.Hg	Atom % Hydrogen
(Au-875°C.)	
403	49.9
559	51.6
605	52.1
(Av-875°C.)	
31	25.3
150	43.4
429	50.0
594	52.2
674	59.6
(Cw-885°C.)	
22	20.0
88	37.3
165	42.9
270	46.5
394	48.5
537	50.5
653	51.1
743	52.5
(Ax-900°C.)	
15	17.1
33	23.3
148	40.6
373	47.4
462	49.2
568	50.2
679	51.0
742	51.6
(Ay-900°C.)	
57	31.1
108	38.2
233	44.5
319	46.9
(Ez-900°C.)	
42	25.7
124	39.0
244	44.6
412	48.3
559	50.2
746	51.4

* Capital letters identify sample used. Lower case letters identify different run

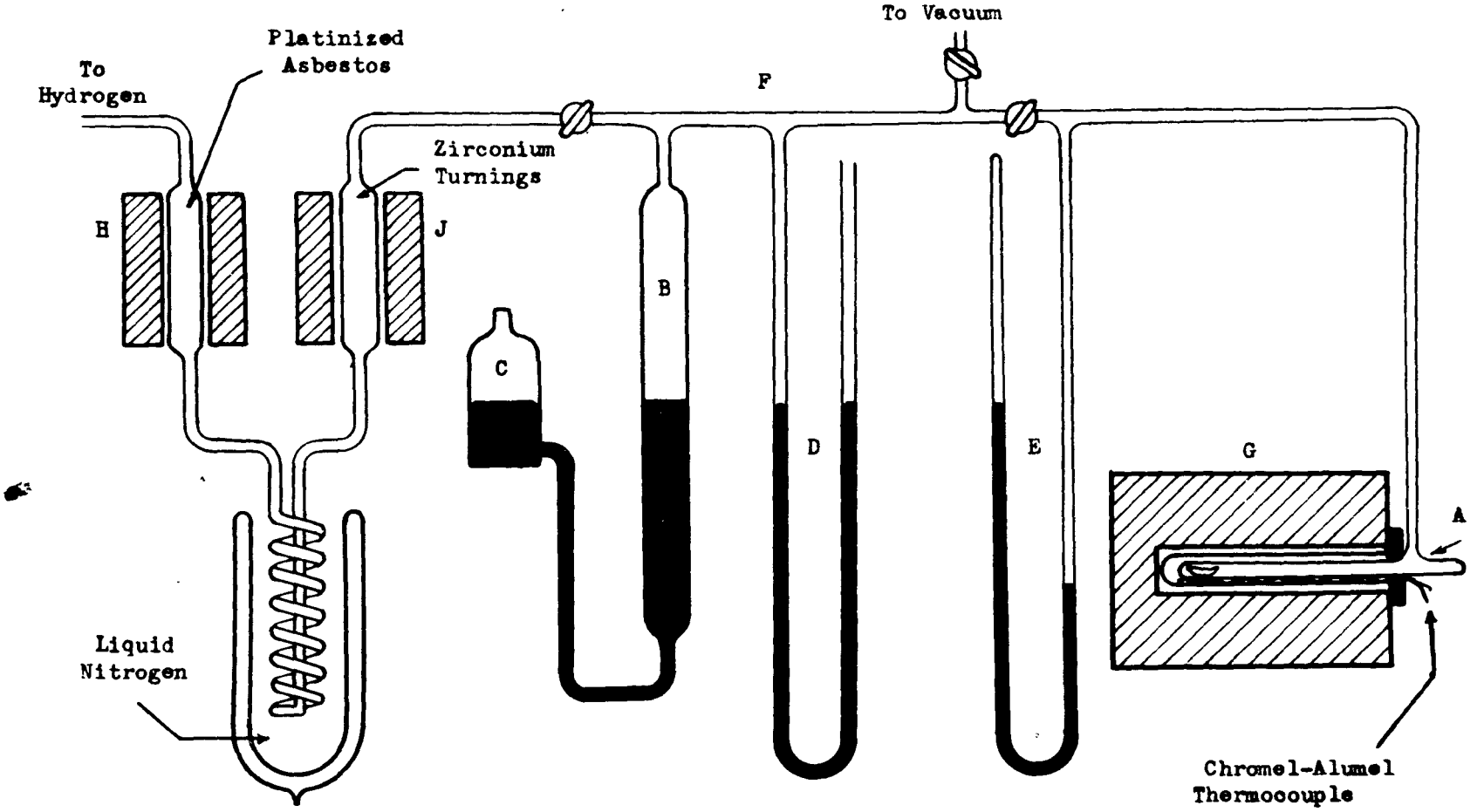

Fig. 1 Apparatus for Studying the Solubility of Hydrogen in Zirconium Metal.

A. Reaction zone, sample boat in place; B. Gas burette (thermometer, water jacket not shown); C. Leveling bulb; D. Open arm manometer; E. Manometer ("closed end" actually to high vacuum); F. Position of thermometer for determining constancy of static gas volume; G. Furnace; H & J. Furnaces, hydrogen purification.

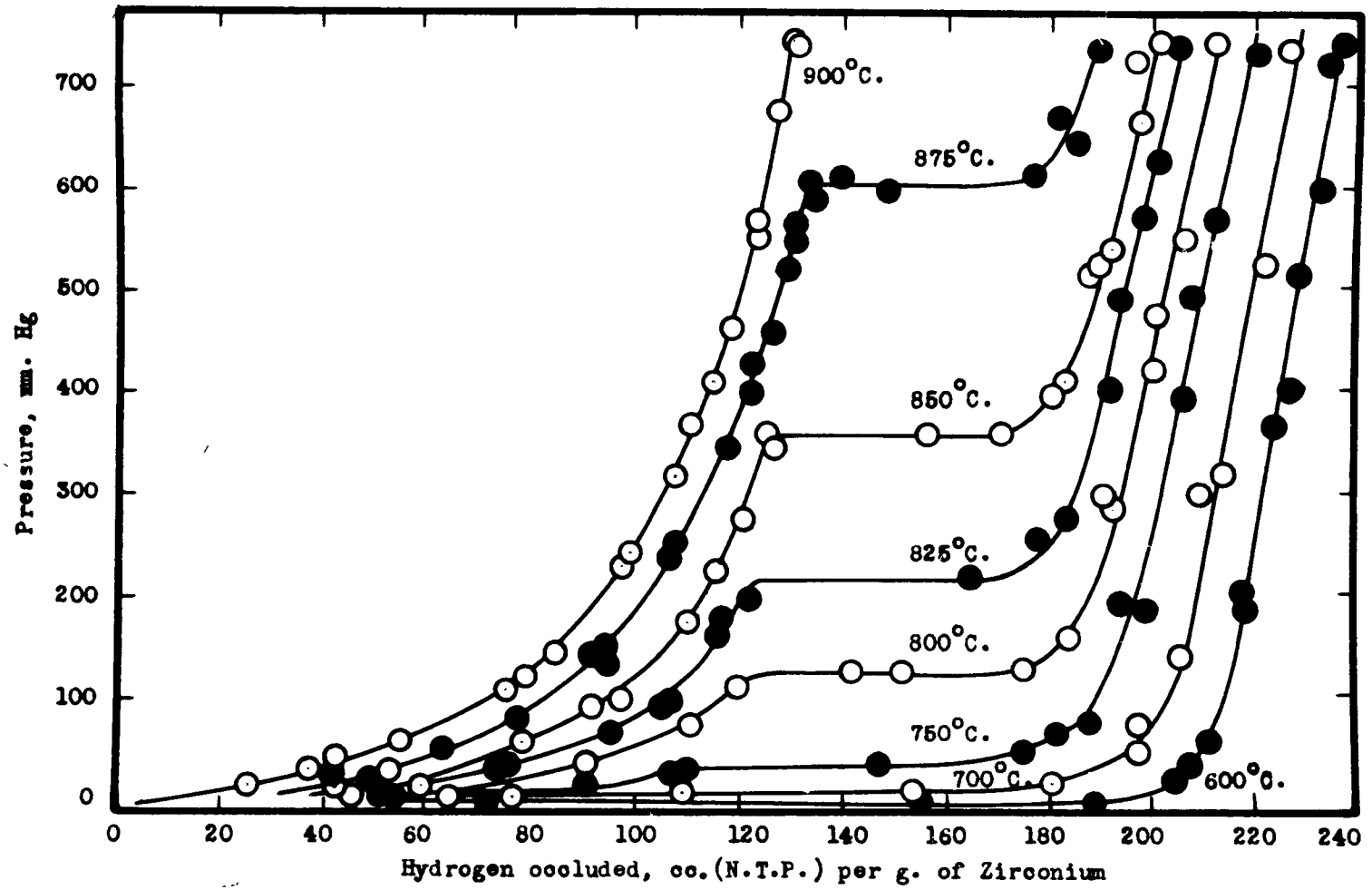

Fig. 2 Isothermal Pressure-Volume Curves for the Temperature Range 600 to 900°C.

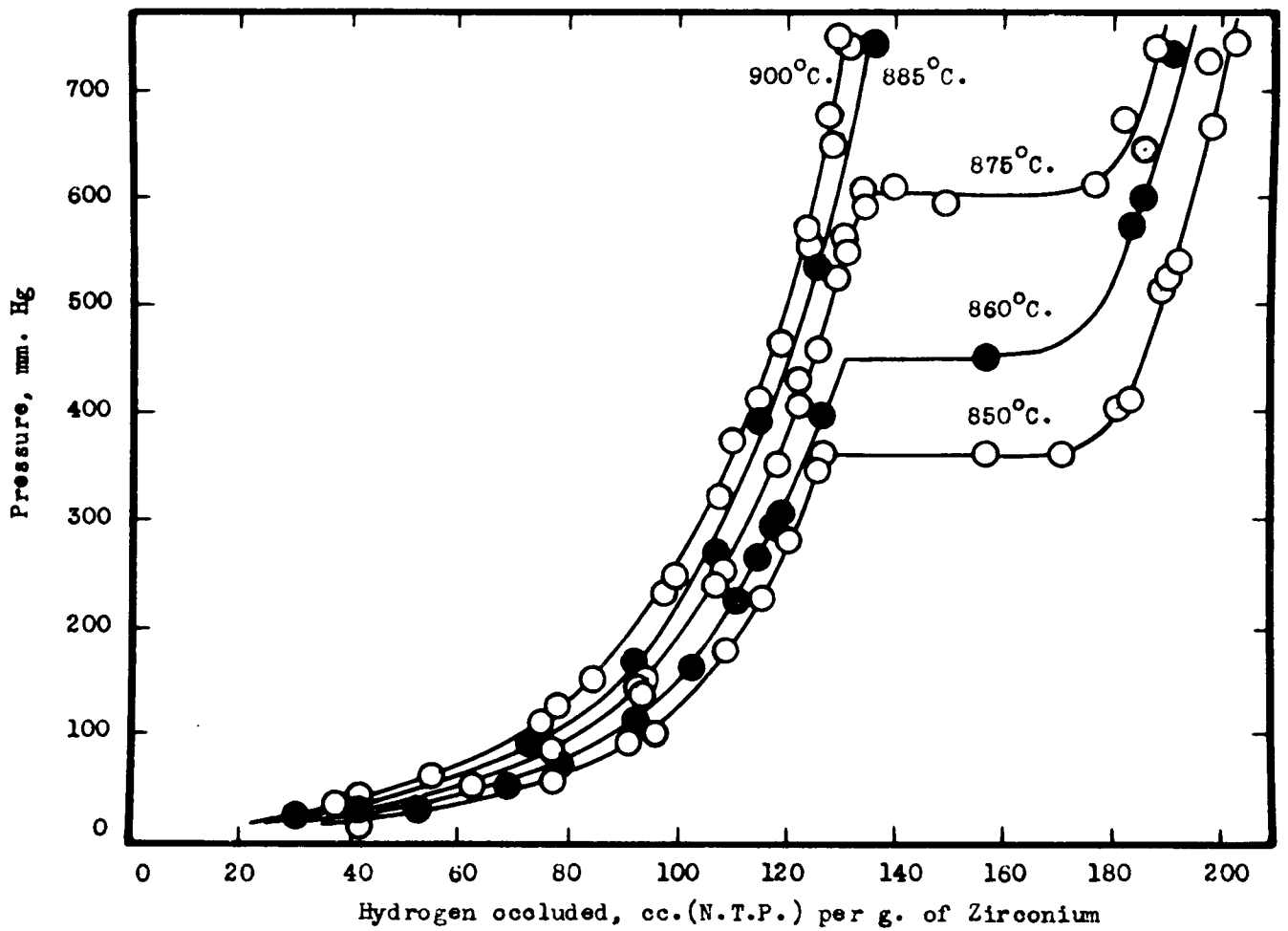

Fig. 3 Isothermal Pressure-Volume Curves for the Temperature Range 850 to 900°C.

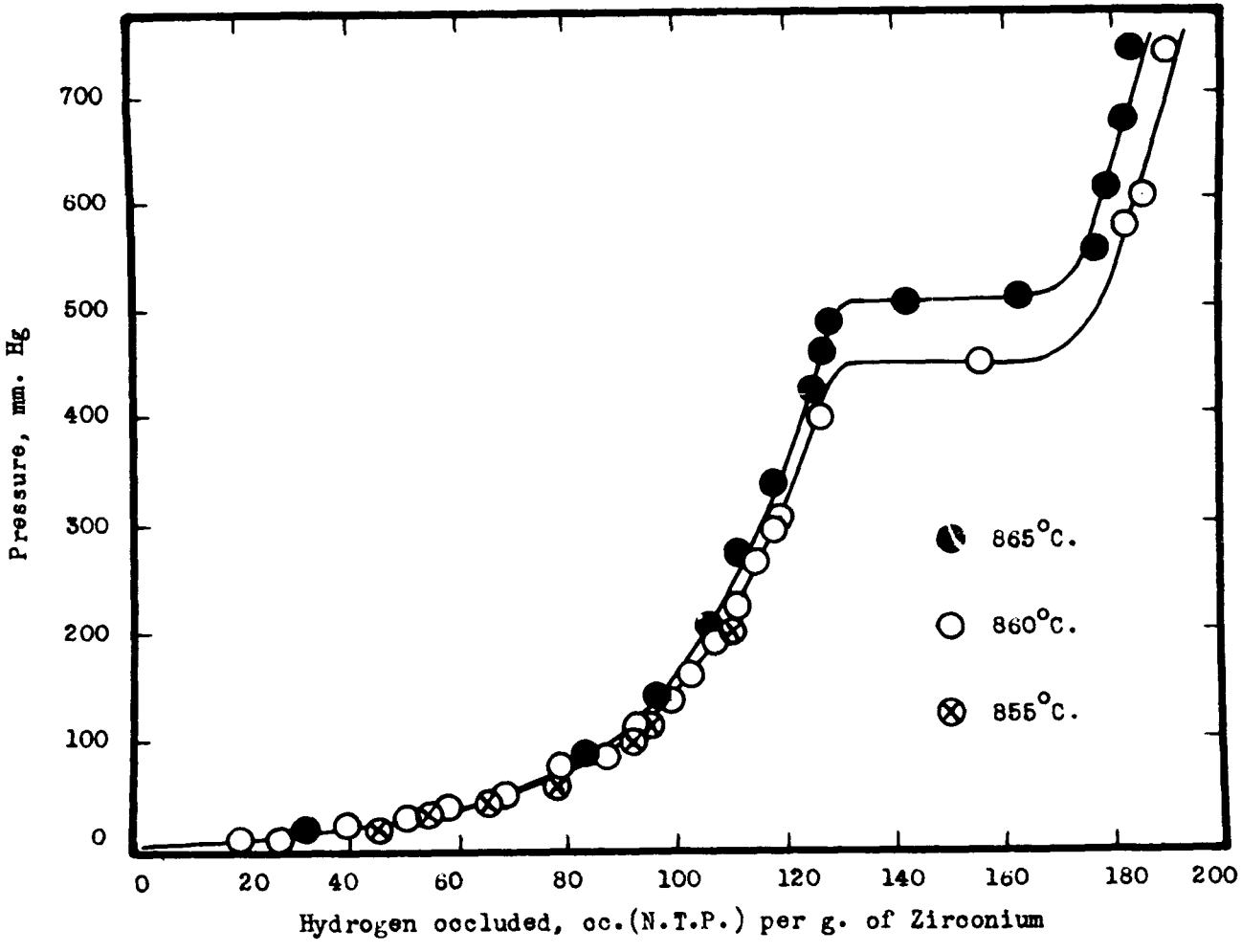

Fig. 4 Isothermal Pressure-Volume Curves for the Temperature Range 855 to 865°C.

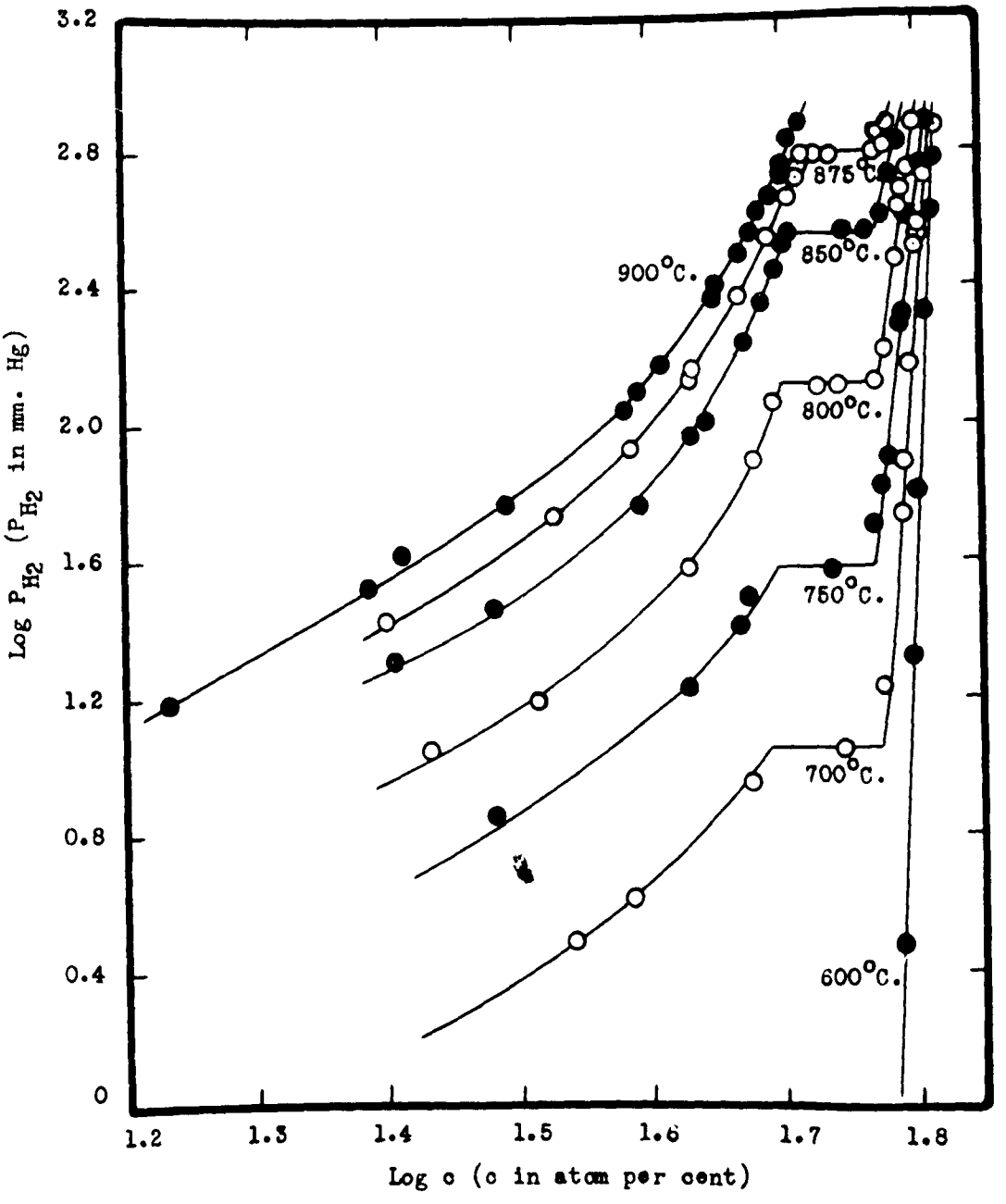

Fig. 5 Isothermal Pressure-Composition Logarithmic Plots for the Temperature Range 600 to 900°C.

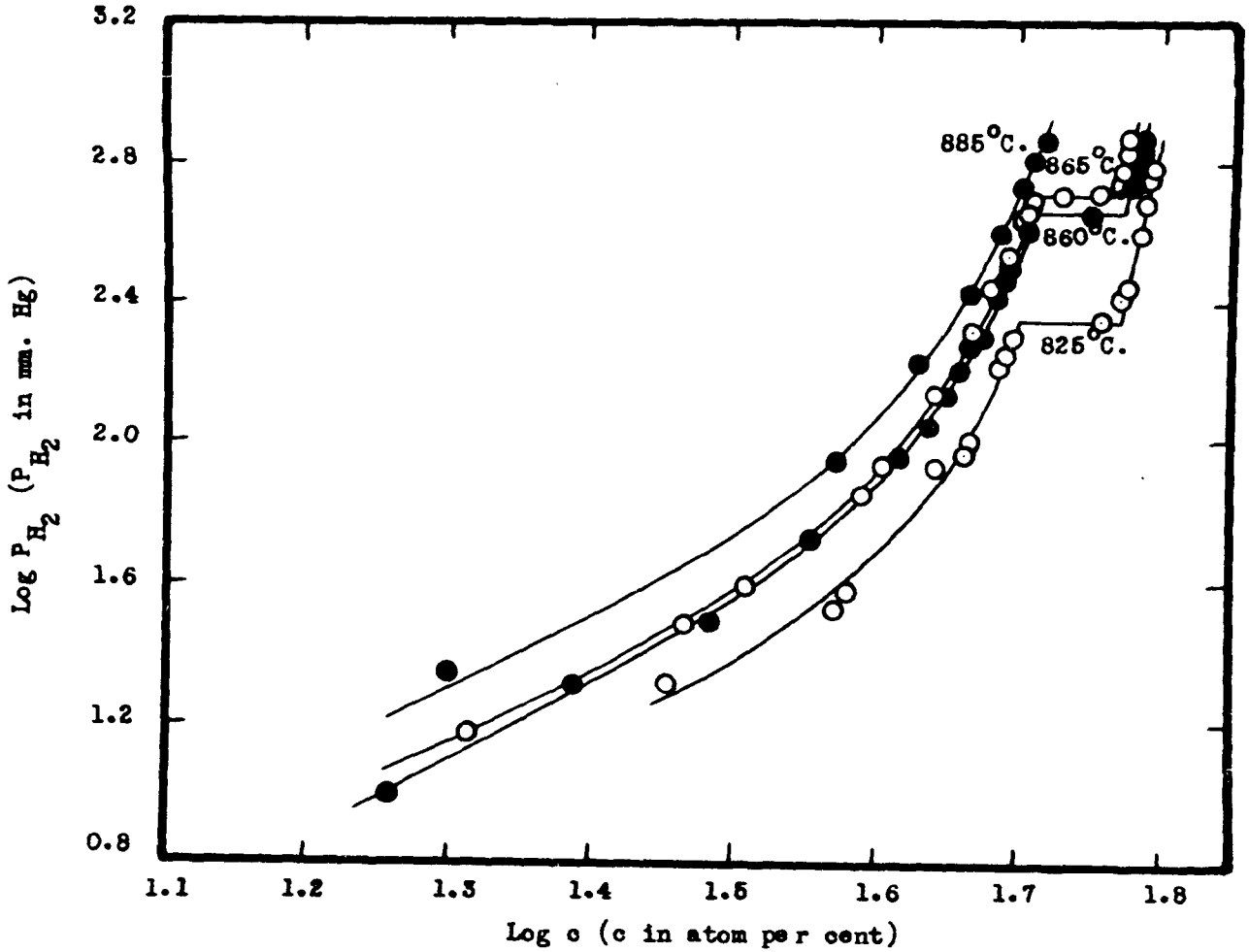

Fig. 6 Isothermal Pressure-Composition Logarithmic Plots for the Temperature Range 825 to 885°C.

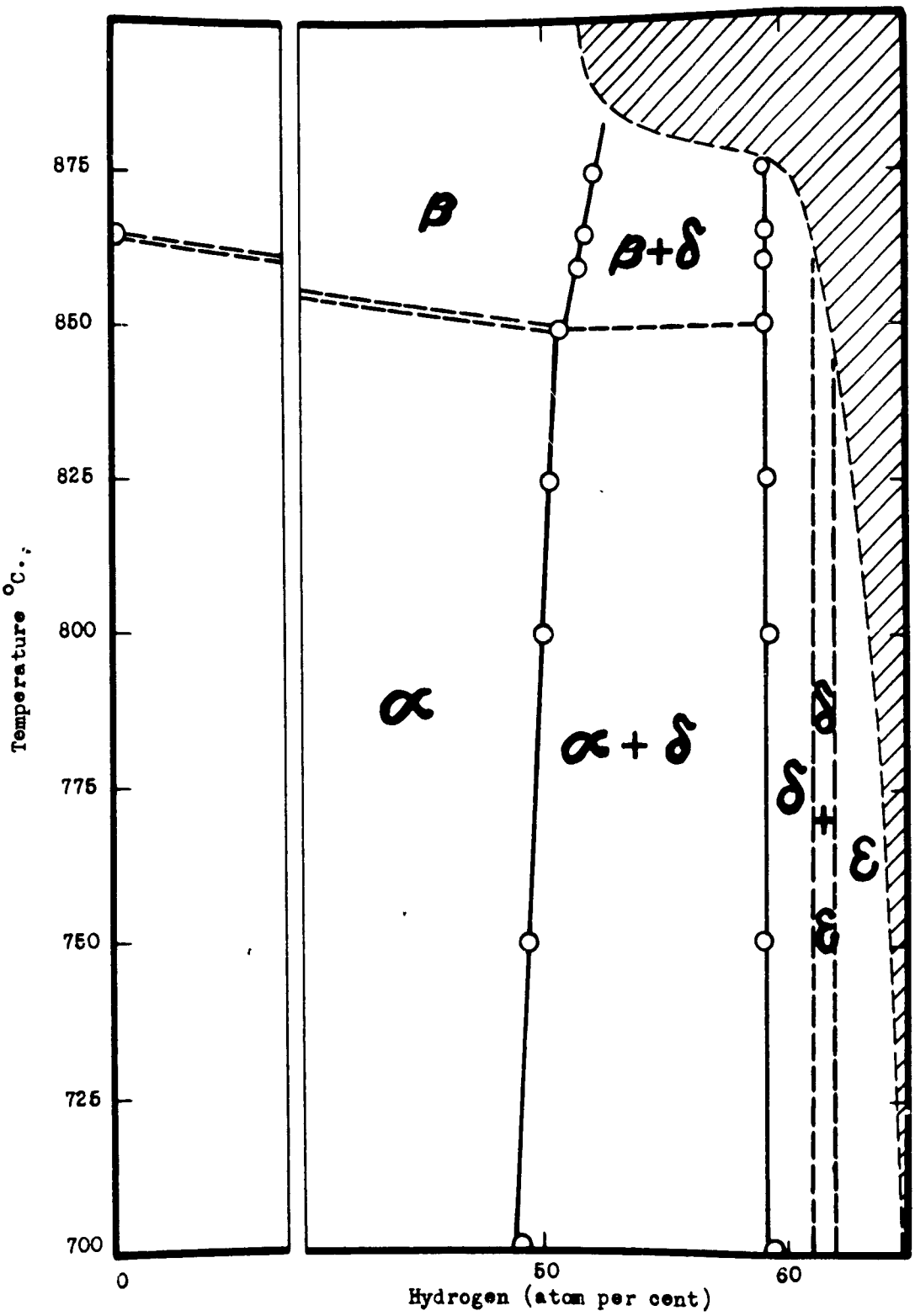

Fig. 7 Partial Phase Diagram of the Zirconium-Hydrogen System.

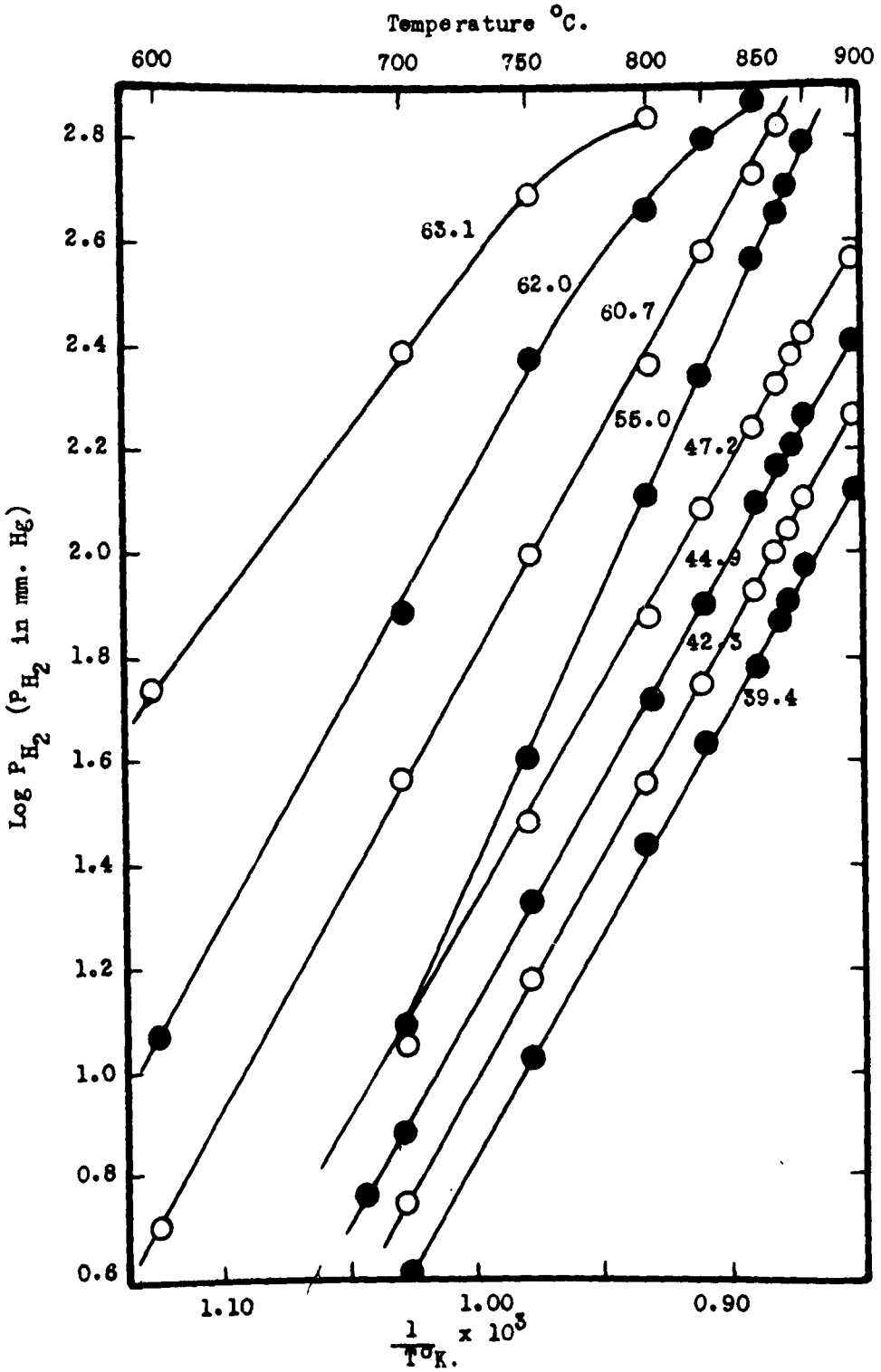

Fig. 8 Pressure-Temperature Curves for the Concentration Range 39.4 to 63.1 Atom Per Cent Hydrogen.